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Multilayer oriented high-modulus film

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MULTILAYER ORIENTED HIGH-MODULUS FILM

The present invention relates to a multilayer oriented film comprising a first outer layer comprising a polyester or co-polyester, a second outer layer comprising one or more ethylene polymers, and a core layer comprising an ethylene-vinyl alcohol
5 copolymer characterized by a high modulus, said film being characterized by a high modulus.

The invention also relates to a process for the manufacture of the new film and to the use of the new film in food packaging.

BACKGROUND OF THE INVENTION

10 Oriented films with a first outer layer of a polyester or copolyester, a second outer layer of a polyethylene, and a core layer of EVOH are known.

EP-A-476,836 for instance describes an oriented laminated film with a surface layer of a PET, an EVOH core layer, an intermediate layer of certain polyamides and a heat-sealing layer of polyolefin, having a specified thickness ratio between the PET and
15 the polyamide layers. The films described there are said to have excellent stretching processability, heat-sealing and packaging properties and good transparency after heat-sterilization.

WO 99/44824 and WO 99/44823 describe EVOH-containing heat-shrinkable films with at least four layers where a first outer layer comprises i.a. a polyethylene and a
20 second outer layer comprises or may comprise a polyester. The bags obtained therefrom can be stacked on top of one another and sealed simultaneously.

WO 01/98081 describes an oriented film, which may comprise a core EVOH layer, and includes a surface layer that may be a polyester and the other surface layer of a sealable resin that may be a polyethylene, characterized by a minimum value of impact
25 strength under certain conditions. These films are said to be particularly suited for certain applications such as freeze packaging, deep drawing packaging, vertical pillow packaging, etc.

In the above documents the process actually described for the manufacture of these films is the so-called trapped bubble process. According to this technique, the polymer feeds are extruded through an annular die to give a thick tubing, called "tape". Said tubing is quickly quenched at the exit of the extrusion die in order to control
5 crystallization, then it is re-heated to the suitably selected orientation temperature and oriented transversely by inflating it with a gas to expand its diameter and longitudinally by running the nip rolls that hold the bubble at a differential speed.

As indicated, the films of these documents are said to have particularly useful properties, but in none of them a particular emphasis has been put on the modulus of the
10 end films and as a matter of fact the modulus of the films described in the above documents does not appear to be particularly high. On the other hand it is widely known that for a good machinability, as well as for a good printability, in most of the currently used packaging systems, the packaging material needs to be stiff, i.e. it should have a high modulus. It would therefore be particularly useful if it were possible to obtain an
15 oriented, shrinkable or non shrinkable, film endowed with good properties, such as those reported in the above quoted prior art documents, coupled however with a high modulus.

Also, the above documents do not contain any indication that oriented heat-shrinkable films with "soft-shrink" characteristics might be obtained, while it is widely known that soft-shrink characteristics, particularly in the transverse direction, would be
20 useful in all the packaging applications where the product to be packaged is sensitive to a high shrink force and in particular it can be crushed or distorted by films with a high shrink force when these films are shrunk around the product. Soft shrink characteristics offer particular utility in food packaging, when a soft product is wrapped into a shrinkable film or loaded into a shrinkable bag or when a tray is wrapped of lidded with
25 a shrinkable material. It would therefore be useful to have an oriented heat-shrinkable film endowed with good properties, such as those reported in the above quoted prior art

documents, which additionally combine a high free shrink with a remarkably low shrink force, particularly in the transverse direction.

It has now been found that it is possible to obtain oriented films with a first outer layer of a polyester or copolyester, a second outer layer of a polyethylene and an inner
5 layer comprising EVOH, which are characterized by a high modulus in at least one direction, by carrying out the orientation of the extruded tape simultaneously in the two directions and by means of a tenter frame.

The films that can thus be obtained, which are characterized by a modulus higher than $6,000 \text{ kg/cm}^2$ in at least one direction, are particularly useful, either as heat-
10 shrinkable or non-shrinkable heat-set films in all the packaging applications where a stiff film is preferred.

It has also been found that the heat-shrinkable films thus obtainable are characterised by a free shrink of at least 10 % in each direction at 120°C and a maximum shrink tension in the transverse direction, in the temperature range of from 20
15 to 180°C of less than 1 kg/cm^2 .

SUMMARY OF THE INVENTION

A first object of the present invention is therefore a multi-layer, bi-axially oriented, thermoplastic film comprising a first outer layer comprising a polyester or a copolyester, a second outer layer comprising an ethylene homo- or co-polymer, and a
20 core layer comprising an ethylene-vinyl alcohol copolymer, said film being characterized by a modulus (evaluated according to ASTM D882) higher than $6,000 \text{ kg/cm}^2$ in at least one direction, preferably higher than $6,500 \text{ kg/cm}^2$ in at least one direction, and more preferably higher than $7,000 \text{ kg/cm}^2$ in at least one direction.

In one embodiment the multi-layer, biaxially oriented, thermoplastic film of the
25 present invention is heat-shrinkable and is also characterised by a free shrink of at least 10 % in each direction at 120°C and by a maximum shrink tension, in the transverse direction, in the temperature range of from 20 to 180°C of less than 1 kg/cm^2 .

In another embodiment the multi-layer bi-axially oriented thermoplastic film of the present invention is a non-shrinkable heat-set film.

A second object is the process for the manufacture of a film of the first object by co-extrusion of the tape followed by its orientation, with an orientation ratio generally
5 comprised between about 2.5 and about 5 in each direction, simultaneously in both directions by means of a tenter frame, said orientation step being optionally followed by an heat-setting step.

A third object of the present invention is the use of a film according to the first object in packaging applications.

10

DEFINITIONS

As used herein, the term "film" is used in a generic sense to include plastic web, regardless of whether it is film or sheet. Typically, films of and used in the present invention have a thickness of 150 μm or less, preferably they have a thickness of 100 μm or less, more preferably a thickness of 75 μm or less, still more preferably a thickness of
15 50 μm or less, and yet, still more preferably, a thickness of 30 μm or less.

As used herein, the phrases "inner layer" and "internal layer" refer to any layer having both of its principal surfaces directly adhered to another layer of the film.

As used herein, the phrase "outer layer" refers to any layer of film having only one of its principal surfaces directly adhered to another layer of the film

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As used herein, the phrase "inside layer" refers to the film outer layer that is closest to the product, relative to the other layers of the multi-layer film.

As used herein, the phrase "outside layer" refers to the film outer layer, of a multi-layer film packaging a product, which is furthest from the product relative to the other layers of the multi-layer film.

25

As used herein, the phrases "seal layer", "sealing layer", "heat seal layer", and "sealant layer", refer to an outer layer involved in the sealing of the film to itself, to another layer of the same or another film, and/or to another article which is not a film. With respect

to packages having only fin-type seals, as opposed to lap-type seals, the phrase "sealant layer" generally refers to the inside layer of a package.

As used herein, the term "core", and the phrase "core layer", refers to any internal layer that preferably has a function other than serving as an adhesive or compatibilizer for adhering two layers to one another.

As used herein, the phrase "tie layer" refers to any internal layer having the primary purpose of adhering two layers to one another. Preferred polymers for use in tie layers include, but are not restricted to, ethylene-unsaturated acid copolymer, ethylene-unsaturated ester copolymer, anhydride-grafted polyolefin, and mixtures thereof.

As used herein, the phrase "machine direction", herein abbreviated "MD", refers to a direction "along the length" of the film, i.e., in the direction of the film as the film is formed during extrusion and/or coating.

As used herein, the phrase "transverse direction", herein abbreviated "TD", refers to a direction across the film, perpendicular to the machine or longitudinal direction.

As used herein, the phrases "orientation ratio" and "stretching ratio" refer to the multiplication product of the extent to which the plastic film material is expanded in the two directions perpendicular to one another, i.e. the machine direction and the transverse direction.

As used herein, the phrases "heat-shrinkable," "heat-shrink," and the like, refer to the tendency of the film to shrink upon the application of heat, i.e., to contract upon being heated, such that the size of the film decreases while the film is in an unrestrained state. As used herein said term refer to films with a free shrink in each direction, as measured by ASTM D 2732, of at least 10 percent at 120 °C.

As used herein, the term "monomer" refers to a relatively simple compound, usually containing carbon and of low molecular weight, which can react to form a polymer by combining with itself or with other similar molecules or compounds.

As used herein, the term "co-monomer" refers to a monomer that is co-polymerized

with at least one different monomer in a co-polymerization reaction, the result of which is a copolymer.

As used herein, the term "polymer" refers to the product of a polymerization reaction, and is inclusive of homo-polymers, and co-polymers.

5 As used herein, the term "homo-polymer" is used with reference to a polymer resulting from the polymerization of a single monomer, i.e., a polymer consisting essentially of a single type of mer, i.e., repeating unit.

As used herein, the term "co-polymer" refers to polymers formed by the polymerization reaction of at least two different monomers. For example, the term "co-
10 polymer" includes the co-polymerization reaction product of ethylene and a α -olefin, such as 1-hexene. However, the term "co-polymer" is also inclusive of, for example, the co-polymerization of a mixture of ethylene, propylene, 1-hexene, and 1-octene. The term "co-polymer" is also inclusive of random co-polymers, block co-polymers, and graft co-polymers.

15 As used herein, terminology employing a "-" with respect to the chemical identity of a copolymer (e.g., "an ethylene- α -olefin copolymer"), identifies the co-monomers which are co-polymerized to produce the copolymer.

As used herein, the phrase "heterogeneous polymer" refers to polymerization reaction products of relatively wide variation in molecular weight and relatively wide
20 variation in composition distribution, i.e., typical polymers prepared, for example, using conventional Ziegler-Natta catalysts. Heterogeneous polymers are useful in various layers of the film used in the present invention. Although there are a few exceptions (such as TAFMER™ linear homogeneous ethylene- α -olefin copolymers produced by Mitsui, using Ziegler-Natta catalysts), heterogeneous polymers typically contain a relatively wide variety
25 of chain lengths and co-monomer percentages.

As used herein, the phrase "homogeneous polymer" refers to polymerization reaction products of relatively narrow molecular weight distribution and relatively narrow

composition distribution. Homogeneous polymers are structurally different from heterogeneous polymers, in that homogeneous polymers exhibit a relatively even sequencing of co-monomers within a chain, a mirroring of sequence distribution in all chains, and a similarity of length of all chains, i.e., a narrower molecular weight distribution. Furthermore, homogeneous polymers are typically prepared using

5 metallocene, or other single-site type catalysts, rather than using Ziegler Natta catalysts.

As used herein, the term "polyolefin" refers to any polymerized olefin, which can be linear, branched, cyclic, aliphatic, aromatic, substituted, or unsubstituted. More specifically, included in the term polyolefin are homo-polymers of olefin, co-polymers of

10 olefin, co-polymers of an olefin and an non-olefinic co-monomer co-polymerizable with the olefin, such as vinyl monomers, modified polymers thereof, and the like. Specific examples include polyethylene homo-polymer, polypropylene homo-polymer, polybutene homo-polymer, ethylene- α -olefin co-polymer, propylene- α -olefin co-polymer, butene- α -olefin co-polymer, ethylene-unsaturated ester co-polymer, ethylene-unsaturated acid co-polymer,

15 (e.g., ethylene-(C₁-C₄)alkyl acrylate or methacrylate copolymers, such as for instance ethylene-ethyl acrylate co-polymer, ethylene-butyl acrylate co-polymer, ethylene-methyl acrylate co-polymer, or ethylene-methyl methacrylate co-polymer, ethylene-acrylic acid co-polymer, ethylene-methacrylic acid co-polymer), ionomer resin, polymethylpentene, etc.

As used herein the term "modified polyolefin" is inclusive of modified polymer

20 prepared by co-polymerizing the homo-polymer of the olefin or co-polymer thereof with an unsaturated carboxylic acid, e.g., maleic acid, fumaric acid or the like, or a derivative thereof such as the anhydride, ester or metal salt or the like. It is also inclusive of modified polymers obtained by incorporating into the olefin homo-polymer or co-polymer, by blending or preferably by grafting, an unsaturated carboxylic acid, e.g., maleic acid, fumaric

25 acid or the like, or a derivative thereof such as the anhydride, ester or metal salt or the like.

As used herein, the phrase "ethylene- α -olefin copolymer" refer to such heterogeneous materials as linear low density polyethylene (LLDPE), linear medium

density polyethylene (LMDPE) and very low and ultra low density polyethylene (VLDPE and ULDPE); and homogeneous polymers such as metallocene-catalyzed homogeneous ethylene- α -olefin copolymer resins and to linear homogeneous ethylene- α -olefin copolymer resins obtainable under homogeneous catalysis conditions but using Ziegler-
5 Natta catalysts (Tafmer® resins by Mitsui). All these materials generally include copolymers of ethylene with one or more co-monomers selected from C₄ to C₁₀ α -olefin such as butene-1, hexene-1, octene-1, etc. in which the molecules of the copolymers comprise long chains with relatively few side chain branches or cross-linked structures. The heterogeneous ethylene- α -olefin copolymer commonly known as LLDPE has a density
10 usually in the range of from about 0.915 g/cm³ to about 0.930 g/cm³, that commonly known as LMDPE has a density usually in the range of from about 0.930 g/cm³ to about 0.945 g/cm³, while those commonly identified as VLDPE or ULDPE have a density lower than about 0.915 g/cm³.

As used herein, the term "adhered" is inclusive of films which are directly
15 adhered to one another using a heat-seal or other means, as well as films which are adhered to one another using an adhesive which is between the two films. As used herein, the phrase "directly adhered", as applied to layers, is defined as adhesion of the subject layer to the object layer, without a tie layer, adhesive, or other layer therebetween. In contrast, as used herein, the word "between", as applied to a layer
20 expressed as being between two other specified layers, includes both direct adherence of the subject layer between to the two other layers it is between, as well as a lack of direct adherence to either or both of the two other layers the subject layer is between, i.e., one or more additional layers can be imposed between the subject layer and one or more of the layers the subject layer is between.

25 As used herein, "EVOH" refers to ethylene/vinyl alcohol copolymer. EVOH includes saponified or hydrolyzed ethylene/vinyl acetate copolymers, and refers to a vinyl alcohol copolymer having an ethylene comonomer, and prepared by, for example,

hydrolysis of vinyl acetate copolymers. The degree of hydrolysis is preferably at least 50%, and more preferably, at least 85%. Preferably, the EVOH comprises from about 28 to about 48 mole % ethylene, more preferably, from about 32 to about 44 mole % ethylene, and even more preferably, from about 38 to about 44 mole % ethylene.

5 As used herein, the term "polyamide" refers to both polyamide homo-polymers and polyamide co-polymers, also called co-polyamides.

 As used herein the term "co-polyamide" on the other hand identifies the polyamide product built from at least two different starting materials, i.e. lactams, aminocarboxylic acids, equimolar amounts of diamines and dicarboxylic acids, in any
10 proportion; this term therefore also encompasses ter-polyamides and, in general, multi-polyamides.

DETAILED DESCRIPTION OF THE INVENTION

 In the film according to the present invention, the first outer layer, that in the use of the film in packaging applications will be the outside layer, comprises a film forming
15 polyester or co-polyester. Suitable film forming polyesters and co-polyesters can be crystalline, semi-crystalline, or amorphous. If crystalline or semi-crystalline, their melting point is preferably comprised between about 100 °C and about 260 °C, and is higher, preferably at least 10 °C higher, and even more preferably at least 20 °C higher, than the melting point of the polyolefin resin of the second outer layer, in order to favor
20 heat-sealability of the film through said second outer layer. The Tg of the film forming polyesters or co-polyesters used for the first outer layer needs to be below 130 °C, in order to allow orientation of the extruded structure at conventional temperatures. Preferably said Tg will be below 110°C, more preferably below 100 °C, and even more preferably below 90 °C.

25 Preferred polyesters and co-polyesters are ring-containing polymers.

 Suitable linear homopolymeric polyesters include poly(ethylene terephthalate), poly(1,2-propylene terephthalate), poly(ethylene 2,5-dimethyl-terephthalate),

poly(butylene terephthalate), poly(ethylene isophthalate), poly(ethylene 5-t-butyl-isophthalate), poly(butylene 2,6-naphthalate), and the like homopolymers.

Suitable copolymers can be random copolymers, i.e. those copolymers where the various components are randomly incorporated into the copolymer chain; alternating or
5 patterned copolymers, i.e. those copolymers whose constituent units stand in a regular pattern of succession along the molecular chains; or block or segmented copolymers.

Examples of dicarboxylic acids that can be included in the copolyester resin are terephthalic acid, isophthalic acid, 2,5-dimethyl-terephthalic acid, 5-t-butyl-isophthalic acid, naphthalene dicarboxylic acid, cyclohexane-dicarboxylic acid, diphenyl ether
10 dicarboxylic acid, sebacic acid, adipic acid, azelaic acid, and the like acids. Examples of diols that can be included in the copolyester resins are ethylene glycol, 1,2-propane-diol, 1,3-propane-diol, 1,4-butanediol, 1,6-hexane-diol, 1,4-cyclohexane-dimethanol, 2,2-bis(4-hydroxyphenyl)propane, and the like.

In the copolyester at least one of the carboxylic acids or of the diols is used in
15 combination of at least two species.

The first outer layer may also comprise a blend of at least two components independently selected from polyesters and copolyesters.

Said layer may also comprise other compatible polymers and/or copolymers blended therein, such as polyamides and copolyamides, polyurethanes, and the like
20 polymers.

Preferably however said first outer layer will comprise at least 70 %, more preferably at least 80 %, and even more preferably at least 90 % by weight calculated on the basis of the overall weight of the layer, of one or more polyesters and/or one or more copolyesters. In a most preferred embodiment said first outer layer will be essentially
25 made of one or more polyesters and/or one or more copolyesters.

Said first outer layer may also contain nucleating agents as known in the art (see for instance Table 1 of the Literature Review by H. Zhou available at the internet address

www.crd.ge.com as 98CRD138). A class of particularly preferred nucleating agents are the inorganic compounds such as talc, silicate, clay, titanium dioxide, and the like. These compounds can be used in an amount of less than 5 % by weight, typically in an amount of 1-2 % by weight on the total weight of the layer. Another class of preferred nucleating agents are certain compatible polymers such as fluoropolymers (PTFE) and the faster crystallising polymers that can be blended with the polyester and/or copolyester of the first outer layer in an amount of up to e.g. 5-10 % by weight.

The thickness of said first outer layer will typically be up to 40 % of the thickness of the overall structure, preferably up to 30 %, more preferably up to 20 % of the overall thickness.

Ethylene homo- and co-polymers suitable for the second outer layer are selected from the group consisting of polyethylene homo-polymers, heterogeneous or homogeneous ethylene- α -olefin copolymers, ethylene-vinyl acetate co-polymers, ethylene-(C₁-C₄) alkyl acrylate or methacrylate co-polymers, such as ethylene-ethyl acrylate co-polymers, ethylene-butyl acrylate co-polymers, ethylene-methyl acrylate co-polymers, and ethylene-methyl methacrylate co-polymers, ethylene-acrylic acid co-polymers, ethylene-methacrylic acid co-polymers, and blends thereof in any proportion.

Preferred ethylene homo- and co-polymers for said second outer layer are e.g. polyethylene homo-polymers having a density of from about 0.900 g/cm³ to about 0.950 g/cm³, heterogeneous and homogeneous ethylene- α -olefin copolymers having a density of from about 0.880 g/cm³ to about 0.945 g/cm³, more preferably of from about 0.885 g/cm³ to about 0.940 g/cm³, yet more preferably of from about 0.890 g/cm³ to about 0.935 g/cm³, and ethylene-vinyl acetate copolymers comprising from about 3 to about 28 %, preferably, from about 4 to about 20 %, more preferably, from about 4.5 to about 18 % vinyl acetate comonomer, and blends thereof.

Even more preferred ethylene homo- and co-polymers for said second outer layer are selected from the group consisting of heterogeneous ethylene- α -olefin copolymers

having a density of from about 0.890 g/cm³ to about 0.940 g/cm³, homogeneous ethylene- α -olefin copolymers having a density of from about 0.890 g/cm³ to about 0.925 g/cm³, ethylene-vinyl acetate copolymers comprising from about 4.5 to about 18 % vinyl acetate comonomer, and blends thereof.

5 In a most preferred embodiment of the present invention the second outer layer comprises a blend of at least two different ethylene- α -olefin copolymers with a density of from about 0.890 g/cm³ to about 0.935 g/cm³, more preferably a blend of a homogeneous and a heterogeneous ethylene- α -olefin copolymer, optionally blended with ethylene-vinyl acetate copolymer.

10 Preferably, the ethylene homo- or co-polymers for said second outer layer have a melt index of from about 0.3 to about 10 g/10 min, more preferably from about 0.5 to about 8 g/10 min, still more preferably from about 0.8 to about 7 g/10 min, even more preferably from about 1 to about 6 g/10 min (as measured by ASTM D1238).

The second outer layer may also comprise a blend of a major proportion of one or
15 more ethylene homo- and/or copolymers with a minor proportion of one or more other polyolefins or modified polyolefins, such as polypropylene homopolymers, propylene-ethylene co-polymers, propylene-ethylene-butene ter-polymers, propylene-ethylene-(C₅-C₁₀)- α -olefin ter-polymers, polybutene homo-polymers, butene-(C₅-C₁₀)- α -olefin copolymers, ionomers, anhydride grafted ethylene- α -olefin copolymers, anhydride
20 grafted ethylene-vinyl acetate copolymers, rubber modified ethylene-vinyl acetate copolymers, and the like.

Said additional polymers may be blended with the ethylene homo- and/or copolymers in said second outer layer in an amount that is typically up to about 40 % by weight, preferably up to about 30 % by weight, more preferably up to about 20 % by
25 weight, and still more preferably up to about 10 % by weight.

The thickness of said second outer layer is generally higher than 10 % of the overall thickness of the structure, preferably higher than 15 % and even more preferably

higher than 20 %, being typically comprised between 20 and 70 %, preferably between 25 and 60 % of the overall thickness of the film.

The film according to the present invention also contains an inner layer, which acts as a gas-barrier layer, comprising an ethylene-vinyl alcohol copolymer.

- 5 The gas-barrier layer - as indicated - may comprise one or more EVOH optionally admixed with one or more polyamide components, as known in the art. As the oxygen permeability of polyamides is generally higher than that of EVOH, the barrier layer will comprise a minor amount of EVOH blended with a major amount of polyamides, whenever medium gas-barrier properties are required, and vice-versa,
- 10 EVOH, possibly blended with a minor amount of polyamides, when high gas barrier properties are required. In particular when high gas-barrier properties are required, said core layer will comprise at least 60 %, preferably at least 70 %, still more preferably at least 80 %, and yet still more preferably at least 90 % by weight of a single EVOH or a blend of two or more EVOHs. Examples of EVOH that may well be employed in the
- 15 production of films according to the present invention are EVAL™ EC F151A or EVAL™ EC F101A, marketed by Marubeni. The possible complement to 100 % in said core gas-barrier layer is typically made of one or more polyamides, either aliphatic or aromatic, such as those commonly indicated as nylon 6, nylon 66, nylon 6/66, nylon 12, nylon 6,12, nylon 6I/6T, nylon MXD6/MXDI, and the like. In such a case a preferred
- 20 polyamide is nylon 6/12, a copolymer of caprolactam with laurolactam, such as GRILON™ CF 6S or GRILON™ W8361 manufactured by EMS, MXD6/MXDI a copolyamide with units from metaxylylendiamine, adipic acid and isophthalic acid, such as GRILON™ FE458 manufactured by EMS or a multipolyamide with monomers from hexamethylenediamine, meta-xylylenediamine, adipic acid and sebacic acid, such as
- 25 GRILON™ XE3569 manufactured by EMS. Other plasticisers and/or other resins compatible with EVOH, as known in the art, can however be present in addition to or alternatively to the polyamide.

Alternatively the possible complement to 100 % in said core gas barrier layer can be made of one or more low molecular weight plasticisers, such as for instance the low molecular weight diols or triols, e.g., 1,2-propanediol, butanediol, propanetriol or pentanediol which are known to increase the stretchability of the EVOH resins.

5 Still alternatively the possible complement to 100 % can be made by blends of polyamides with low molecular weight plasticisers.

In a most preferred embodiment however the core gas-barrier layer will essentially consist of EVOH as the gas barrier properties of the 100 % EVOH are much higher than those of the blended EVOH.

10 The thickness of said barrier layer will depend on the barrier properties desired for the end film. More particularly its thickness will be set in order to provide the overall multi-layer film with the desired Oxygen Transmission Rate (OTR) (evaluated by following the method described in ASTM D-3985 and using an OX-TRAN instrument by Mocon). For high gas barrier films an OTR lower than 50, preferably lower than 10,
15 and even more preferably lower than $5 \text{ cm}^3/\text{m}^2 \cdot \text{d} \cdot \text{atm}$, when measured at 23 °C and 0 % of relative humidity is generally required. Typically, when EVOH is employed as the gas-barrier material, optionally blended with up to 20 % by weight of a polyamide, this is achieved with barrier layers 2 to 6 μm thick. Thicker or thinner EVOH containing layers may however be employed depending on the barrier properties required and on the
20 particular composition of said EVOH containing layer.

Additional layers, such as for instance "bulk" layers or "structural" layers, i.e. layers generally of polymers which are inexpensive relative to other polymers in the film and that may be used to improve the abuse or puncture resistance of the film or just to provide the desired thickness, may be present. Polymers suitable for these layers are
25 typically ethylene homo- and co-polymers, e.g. low density polyethylene, ethylene-vinyl acetate copolymers, linear low density polyethylenes and linear very low density

polyethylenes. The thickness of the bulk layers that may possibly be present in the overall structure will depend mainly on the overall thickness desired for the film.

Other layers that may be present in the multi-layer film of the invention are tie or adhesive layers that are employed to better adhere one layer to another in the overall structure.

In particular the film may include a tie layer directly adhered (i.e., directly adjacent) to one or both sides of the core gas-barrier layer. While in most of the embodiments a tie layer improving the adhesion between the core EVOH-containing gas-barrier layer and the heat-sealable second outer layer is required, in some instances this is not necessary and the two layers can adhere with a sufficient bond even in the absence of an intermediate tie layer. As an example when the heat-sealable second outer layer comprises ethylene-vinyl acetate, optionally blended with modified ethylene vinyl acetate, it is not necessary to provide for a tie layer between said layer and the core EVOH-containing one. Tie layers may also be used, in case of bulk layers, to better adhere said layers to the adjacent ones, e.g. the first outer layer or the second outer layer.

Tie layers may include polymers having grafted polar groups so that the polymer is capable of covalently bonding to polar polymers. Useful polymers for tie layers include ethylene-unsaturated acid copolymers, ethylene-unsaturated ester copolymers, anhydride-modified polyolefins, polyurethane, and mixtures thereof. Preferred polymers for tie layers include one or more of thermoplastic polymers such as ethylene-vinyl acetate copolymers with high vinyl acetate content (e.g. 18- 28 wt. % or even more), ethylene-(meth)acrylic acid copolymers, ethylene homo-polymers or co-polymers, such as LDPE, LLDPE or EVA, modified with anhydride or carboxylic acid functionalities, blends of these resins or blends of any of the above resins with an ethylene homo- or co-polymer, and the like known resins.

The tie layers are of a sufficient thickness to provide the adherence function, as is known in the art. Their thickness however is generally kept as low as possible in view

of the high cost of these resins. Typically they will be from about 1, preferably about 2, to about 10, preferably about 8 μm . While layers thinner than 1 μm are generally not sufficient to provide the desired adherence, tie layers thicker than 10 μm may well be employed but without providing a further increase in the bond properties.

5 When two or more tie layers are present in the overall structure, each one may be of a substantially similar or of a different composition and/or thickness.

 The film of the present invention may also contain an oxygen scavenger layer positioned between the gas-barrier core layer and the second outer layer. Preferred oxygen scavengers are made of the combination of an oxidizable polymer, such as any
10 ethylenically unsaturated hydrocarbon polymer, and a transition metal catalyst, but any other scavenging system may be contemplated and typically inert polymers such as polyolefins are used as the diluent.

 In a preferred embodiment of the present invention tie layers are present between the core gas-barrier layer and each of the first and second outer layers. Preferred polymers
15 for use in said tie layers are anhydride grafted ethylene-vinyl acetate and anhydride grafted ethylene- α -olefin copolymers that may be blended with one or more polyolefins.

 In one embodiment the film of the present invention has three layers, the first and second outer layers and the core EVOH containing layer. In this embodiment the composition of the outer layers will be suitably devised in order to provide for the
20 necessary adherence between the layers.

 In another embodiment the film has four layers with a tie layer positioned between any one of the first and second outer layers and the core layer.

 In still another, preferred, embodiment, the film has five layers with a first tie layer positioned between the first outer layer and the core barrier layer and a second tie
25 layer positioned between the second outer layer and the core barrier layer.

 In all the film layers, not only in the outer layers, the polymer components may contain appropriate amounts of additives normally included in such compositions. These

include slip and anti-block agents such as talc, waxes, silica, and the like, antioxidants, fillers, pigments and dyes, cross-linking inhibitors, cross-linking enhancers, UV absorbers, antistatic agents, anti-fog agents or compositions, and the like additives known to those skilled in the art of packaging films.

- 5 Preferably, the film of the present invention has an overall thickness of from about 10 to about 60 μm , more preferably, from about 12 to about 50 μm , and, still more preferably, from about 14 to about 40 μm .

10 The film according to the present invention is obtained by melt extruding the polymers or polymer blends used for each layer through a flat die, cooling quickly the multi-layer sheet exiting from the extrusion die by means of a chill roll, optionally irradiating the cast sheet thus obtained to get cross-linking, reheating this flat tape to the suitably selected orientation temperature, simultaneously stretching the heated tape in both directions, MD and TD, at a stretching ratio higher than 2.5:1, preferably higher than 3:1, in each direction, by any simultaneous tenter apparatus, optionally stabilizing
15 the obtained bi-axially oriented heat-shrinkable film by an annealing or an heat-setting step and finally cooling the thus obtained bi-axially oriented, high modulus, multi-layer film thus obtained.

20 It has been found in fact that it is necessary to employ a simultaneous orientation technique in order to get a biaxial orientation of at least 2.5:1 in each direction in a tape with a first outer layer comprising a polyester or copolyester, a second outer layer comprising an ethylene homo- or co-polymer, and a core layer comprising an ethylene-vinyl alcohol copolymer, and that by using the simultaneous tenter frame orientation technique it is possible to obtain a bi-axially oriented film characterized by a modulus in at least one direction which is higher than that achievable with the trapped bubble technique. More
25 particularly it has been found that by using the simultaneous tenter frame technique in the orientation step it is possible to obtain an oriented film, heat-shrinkable or heat-set, comprising a first outer layer comprising a polyester or a copolyester, a second outer

layer comprising an ethylene homo- or co-polymer, and a core layer comprising an ethylene-vinyl alcohol copolymer, characterized by a modulus higher than $6,000 \text{ kg/cm}^2$ in at least one direction. The film that can be obtained by this technique, is preferably characterized by a modulus higher than $6,500 \text{ kg/cm}^2$ in at least one direction, and more preferably higher than $7,000 \text{ kg/cm}^2$ in at least one direction. In a more preferred embodiment the film obtained by the above process has a modulus higher than $6,000 \text{ kg/cm}^2$ in both directions.

It has also been found that by using the simultaneous tenter frame technique it is also possible to obtain a bi-axially oriented heat-shrinkable film with a maximum shrink tension in the transverse direction, in the temperature range of from 20 to 180°C , of less than 1 kg/cm^2 . It has also been found that such a low shrink tension value in the transverse direction can also be obtained with heat-shrinkable films showing a high free shrink, e.g., films with a total free shrink of 40% , 50% , 60% , or even more.

A second object of the present invention is therefore a process for manufacturing a bi-axially oriented, thermoplastic, multi-layer film comprising a first outer layer comprising a polyester or a copolyester, a second outer layer comprising an ethylene homo- or co-polymer, and a core layer comprising an ethylene-vinyl alcohol copolymer, and characterized by a modulus higher than $6,000 \text{ kg/cm}^2$ in at least one direction, which process comprises co-extrusion of the film resins through a flat die and bi-axial orientation of the obtained cast sheet simultaneously in the two perpendicular directions at an orientation ratio in the longitudinal direction higher than $2.5:1$, preferably higher than $3:1$ and at an orientation ratio in the cross-wise direction higher than $2.5:1$, preferably higher than $3:1$, by means of a tenter frame.

The process according to the present invention involves feeding the solid polymer or polymer blend beads for at least the core gas-barrier layer and the first and second outer layers to the extruders, where the polymer beads are melted and then forwarded into a flat extrusion die where the molten resins of the layers are combined to give the desired

sequence. The obtained tape, that is preferably from about 0.1 mm to about 2 mm thick, is then cooled, either by means of a chill roll, typically with the aid of an air knife that keeps the sheet in contact with the chill roll, or by using a liquid-knife as described in WO-A-95/26867 where a continuous and substantially uniform layer of water or of any other
5 cooling liquid flows onto the surface of the sheet that does not contact the chill roll. Any other known means for cooling the cast web can however be employed.

The cooled sheet is then optionally fed through an irradiation unit, typically comprising an irradiation vault surrounded by a shielding. The flat sheet may in fact be irradiated with high energy electrons (i.e., ionizing radiation) from an iron core transformer
10 accelerator. Irradiation is carried out to induce cross-linking. The flat sheet is preferably guided through the irradiation vault on rolls. It is thus possible by suitably combining the number of rolls and the path of the traveling web within the irradiation unit to get more than one exposure of the sheet to the ionizing radiation. In one embodiment, the sheet is irradiated to a level of from about 10 to about 200 kGy, preferably of from about 15 to
15 about 150 kGy, and more preferably of from about 20 to about 120 kGy, wherein the most preferred amount of radiation is dependent upon the polymers employed and the film end use. While irradiation is preferably carried out on the extruded cast sheet just before orientation, as described above, it could also be carried out, alternatively or additionally, during or after orientation.

20 The optionally irradiated tape is then fed to the pre-heating zone of a simultaneous tenter apparatus, with or without a prior passage through an IR heated oven. The temperature of the oven in said pre-heating zone, the length thereof and the time spent by the traveling web in said zone (i.e. the web speed) can suitably be varied in order to bring the sheet up to the desired temperature for bi-axial orientation. In a preferred embodiment
25 the orientation temperature is comprised between about 100 °C and about 140 °C and the temperature of the pre-heating zone is kept between about 110 °C and about 150 °C. In said pre-heating zone the sheet is clipped but it is not yet stretched. Thereafter, the resulting hot,

optionally irradiated, and clipped sheet is directed to the stretching zone of the simultaneous tenter. Any stretching means can be used in said zone, provided a simultaneous stretching of the sheet in the machine and the transverse direction is obtained. Preferably however the clips are propelled throughout the opposed loops of the tenter frame by means of a linear synchronous motor. A suitable line for simultaneous stretching with linear motor technology has been designed by Brückner GmbH and advertised as LISIM® line. An alternative line for simultaneous stretching of the extruded flat tape is the DMT line, based on a pantograph, equipped with two separated monorails on each side of the orientation unit. The configuration of the tenter can be varied depending on the stretching ratios desired. The stretching ratios that are applied are generally comprised between about 2.5:1 and about 5:1 for MD stretching and between about 2.5:1 and about 5:1 for TD stretching. Preferably however stretching ratios higher than 2.5:1 in both directions are applied, wherein stretching ratios higher than 3:1 are more preferred. The temperature in the stretching zone is kept close to the selected orientation temperature. The stretched film is then transferred in a zone that, depending on whether a heat-shrinkable or non-shrinkable film is desired, may be a relaxation/annealing or heat-setting zone, heated to a temperature of about 70-90 °C, or 110-120°C respectively. Following said annealing or heat-setting step the film is transferred to a cooling zone where generally air, either cooled or kept at the ambient temperature, is employed to cool down the film. The temperature of said cooling zone is therefore typically comprised between about 20 and about 40 °C. At the end of the line, the edges of the film, that were grasped by the clips and have not been oriented, are trimmed off and the obtained bi-axially oriented, heat-shrinkable or heat-set film is then wound up, with or without prior slitting of the film web to the suitable width.

The bi-axially oriented film of the present invention, when heat-shrinkable, may have a total free shrink, at 120 °C, of from about 20 to about 170 percent, preferably from about 30 to about 160 percent, more preferably from about 40 to about 150 percent, still more preferably from about 50 to about 140 percent, and still more preferably from

about 60 to about 130 percent.

As indicated above the bi-axially oriented heat-shrinkable film of the present invention, is also characterised by a maximum shrink tension in at least the transverse direction, in the temperature range of from 20 to 180 °C of less than 1 kg/cm².

5 The biaxially oriented film of the present invention, when heat-set, will have a total free shrink, at 120 °C, lower than 20 percent, preferably lower than 15 percent, more preferably lower than 10, and even more preferably lower than 6 %.

The film thus obtained has a thickness variation of less than 10 percent, preferably less than 8 percent, and more preferably less than 5 percent.

10 The obtained film may then be subjected to a corona discharge treatment to improve the print receptivity characteristics of the film surface. As used herein, the phrases "corona treatment" and "corona discharge treatment" refer to subjecting the outer surfaces of the film to a corona discharge treatment, i.e., the ionization of a gas such as air in close proximity to a film surface, the ionization initiated by a high voltage passed through
15 a nearby electrode, and causing oxidation and other changes to the film surface, such as surface roughness. Corona treatment of polymeric materials is disclosed in e.g. US-A-4,120,716.

The obtained film may also be coated with e.g. an antifog composition, with or without a binder to incorporate the antifog additive into the film; a liquid smoke; an aroma
20 transfer composition; an antibacterial or anti-mould composition; etc. as known in the field.

The invention is further illustrated by the following examples, which are provided for the purpose of representation, and are not to be construed as limiting the scope of the invention. Unless stated otherwise, all percentages, parts, etc. are by weight.

Example 1

25 A five-layer, heat-shrinkable film with the following layer arrangement (C)/(D)/(A)/(D)/(B), a total thickness of 25 µm, and a thickness ratio of 4/1/1/1/1.3 is produced by the general process described above. In particular, the temperature of the

- chill roll is kept at 15-25 °C and the extruded sheet is pinned to the chill roll by means of an air knife. The thickness of the cast extruded sheet before orientation is about 0.4 mm and the linear speed of the quenched sheet is about 8 m/min. The sheet is not irradiated. The temperature in the pre-heating zone is kept between about 120 and about 130 °C.
- 5 The stretching ratios applied are 4:1 in MD and 4:1 in TD and the temperature in the stretching zone is maintained between about 110 and about 120 °C. The annealing step is carried out at about 80-85 °C and the cooling step at about 30-35 °C. After cooling, the film edges are trimmed off and the film is wound onto a roll at a speed of about 36 m/min.
- 10 The resins employed for the various layers were as follows:
- (A) ethylene-vinyl alcohol copolymer containing 44 % of ethylene (EVAL™ E151B from Marubeni);
 - (B) 50 % of a heterogeneous ethylene-octene copolymer with a density of 0.920 g/cm³ and a melt index of 1.0 g/10 min (Dowlex™ 2045 by Dow);
 - 15 25 % of a heterogeneous ethylene-octene copolymer with a density of 0.935 g/cm³ and a melt index of 2.6 g/10 min (Dowlex™ SC 2108 by Dow);
 - 15 % of homogeneous ethylene-octene copolymer with a density of 0.902 g/cm³ and a melt index of 1.0 g/10 min (Affinity™ PL1845 by Dow);
 - 10 % of a master-batch based on ethylene-vinyl acetate copolymer (3.5 % of vinyl acetate content) containing slip (3 %) and anti-block (0.9 %) agents;
 - (C) PETG with Tg 81 °C (Estar 6763 by Eastman);
 - (D) homogeneous ethylene- α -olefin copolymer (Tafmer™ like) with d = 0.906 g/cm³ and MFI = 1.5 g/10', modified with maleic anhydride (m.p. 116°C) (ADMER™ AT1094E by Mitsui)
- 25 The modulus of the obtained structure is 6,400 kg/cm² in LD and 7,000 kg/cm² in TD.
- The free shrink at 120 °C is 43 % in LD and 50 % in TD.

The shrink force was evaluated by the method described hereinbelow in the temperature range of from 20 to 180 °C and the maximum shrink tension thus determined was 0.14 kg/cm² in TD (at 113 °C) and 0.21 kg/cm² in LD (at 110 °C) :

specimens of the films (2.54 cm x 14.0 cm) are cut in the longitudinal and
 5 transverse directions and clamped between two jaws, one of which is connected to a load cell. The two jaws keep the specimen in the center of a channel into which an impeller blows heated air and three thermocouples measure the temperature. The signal supplied by the thermocouples is amplified and sent to an output connected to the "X" axis of an X/Y recorder. The signal supplied by the load cell is also amplified and sent to the "Y" axis of
 10 the X/Y recorder. The impeller starts blowing hot air and the force released by the sample is recorded in grams. As the temperature increases the measured profile of the shrink force versus the temperature will be drawn on the X/Y recorder. When the temperature of 180 °C is reached, the heater is turned off, the specimen temperature gradually reduces and the profile of the shrink force under negative temperature gradients (cooling) is recorded.

15 The instrument produces a curve of the shrink force (g) versus temperature (°C); dividing the value by the specimen width, shrink force in kg/cm is obtained and further dividing by the specimen thickness the shrink tension, in kg/cm², is obtained.

Example 2

A five-layer, heat-shrinkable film with essentially the same layer arrangement as
 20 in Example 1 but with PET (PET18696 by Eastman Chemical) replacing the PETG in layer (C), and with a thickness ratio of 5/1/1/1/1.5 is produced by the same process described in Example 1 with the only difference that the stretching ratio was 3:1 in the longitudinal direction and 3.5:1 in the transverse direction.

A film with a thickness of 25 µm was obtained characterized by a modulus of
 25 7,000 kg/cm² in LD and 9,000 kg/cm² in TD.

The film had a free shrink of 15 % in LD and 55 % in TD at 120 °C and a shrink tension of 0 kg/cm² in TD and 1.20 kg/cm² in LD (at 105 °C)

Example 3

A five-layer, heat-shrinkable film with the same layer arrangement and thickness ratio as in Example 1 is produced by the same process there described with the only difference that the cast sheet is irradiated before orientation to 45 kGray by means of a scan beam unit operated at 500 kVolt and the sheet is passed twice under the irradiation window to provide for a uniform cross-linking.

Example 4

The process of Example 1 has been repeated with the only difference that instead of annealing at a temperature of 85-90°C, the bi-axially oriented film is heat-set at a temperature of 110-120 °C by reducing the line speed by 20 % and allowing the stretching clips to converge by 20 %.

The obtained film showed a total free shrink at 120 °C lower than 5 %.

Example 5

The process of Example 2 has been repeated with the only difference that instead of annealing at a temperature of 85-90°C, the bi-axially oriented film is heat-set at a temperature of 110-120 °C by reducing the line speed by 20 % and allowing the stretching clips to converge by 20 %.

The obtained film showed a total free shrink at 120 °C lower than 5 %.

The films obtained according to the present invention can be used in the packaging of food and non food, oxygen-sensible, products as known in the art. To this purpose they can be used as such in the form of a film or laminate and either wrapped up around the product or employed as a lid for any suitable container such as a tray, or they may be first converted into flexible containers, such as bags or pouches, by conventional techniques well known to the person skilled in the art. They can also be coupled or laminated to other films or sheets to obtain a packaging material of improved performance.

In a most preferred embodiment the biaxially oriented non heat-shrinkable films of

the present invention can conveniently be employed in all those processes that actually use sheets of biaxially oriented polyester (BO-PET) glue-laminated to a heat-sealable barrier film. While the performance of the films of the present invention in these packaging processes is at least comparable to that obtained with the conventional laminates because of

5 the remarkable stiffness of the films of the present invention, the process for the manufacture thereof is much easier and much more convenient as any lamination step may be avoided, as well as the use of any glue and solvent involved therein.

Although the present invention has been described in connection with the preferred embodiments, it is to be understood that modifications and variations may be

10 utilized without departing from the principles and scope of the invention, as those skilled in the art will readily understand. Accordingly, such modifications may be practiced within the scope of the following claims.

CLAIMS

1. A multi-layer, bi-axially oriented, thermoplastic film comprising a first outer layer comprising a polyester or a copolyester, a second outer layer comprising an ethylene homo- or co-polymer, and a core layer comprising an ethylene-vinyl alcohol copolymer, said film being characterized by a modulus higher than 6,000 kg/cm² in at least one direction, preferably higher than 6,500 kg/cm² in at least one direction, and more preferably higher than 7,000 kg/cm² in at least one direction.
2. The multi-layer, biaxially oriented, thermoplastic film of claim 1 characterized by a modulus higher than 6,000 kg/cm² in both directions.
3. The multi-layer, biaxially oriented, thermoplastic film of claim 1 which is heat-shrinkable and is characterized by a maximum shrink tension in the transverse direction, in the temperature range of from 20 to 180 °C, of less than 1 kg/cm².
4. The multi-layer, biaxially oriented, thermoplastic film of claim 3 which has a total free shrink, at 120 °C, of from about 20 to about 170 percent, preferably from about 30 to about 160 percent, more preferably from about 40 to about 150 percent, and still more preferably from about 50 to about 140 percent.
5. The multi-layer, biaxially oriented, thermoplastic film of claim 1 which is non-shrinkable and heat-set and is characterized by a total free shrink, at 120 °C, lower than 20 percent, preferably lower than 15 percent, more preferably lower than 10, and even more preferably lower than 6 %.
6. The multi-layer, biaxially oriented thermoplastic film of any of the preceding claims wherein the polyester or copolyester of the first outer layer is a ring-containing polymer.
7. The multi-layer, biaxially oriented thermoplastic film of claim 5 wherein the polyester is selected from the group consisting of poly(ethylene terephthalate), poly(1,2-propylene terephthalate), poly(ethylene 2,5-dimethyl-terephthalate),

poly(butylene terephthalate), poly(ethylene isophthalate), poly(ethylene 5-t-butyl-isophthalate), poly(butylene 2,6-naphthalate), and the like homopolymers.

8. The multi-layer, biaxially oriented thermoplastic film of claim 5 wherein the copolyester comprises at least one of the carboxylic acids selected from
5 terephthalic acid, isophthalic acid, 2,5-dimethyl-terephthalic acid, 5-t-butyl-isophthalic acid, naphthalene dicarboxylic acid, cyclohexane-dicarboxylic acid, diphenyl ether dicarboxylic acid, sebacic acid, adipic acid, azelaic acid, and the like acids used with at least one of the diols selected from ethylene glycol, 1,2-propane-diol, 1,3-propane-diol, 1,4-butanediol, 1,6-hexane-diol, 1,4-
10 cyclohexane-dimethanol, 2,2-bis(4-hydroxyphenyl)propane, and the like, and where at least one of the carboxylic acids or of the diols is used in combination of at least two species.
9. The multi-layer, biaxially oriented thermoplastic film of any of the preceding claims wherein the ethylene homo- and co-polymers of the second outer layer are
15 selected from the group consisting of polyethylene homo-polymers, heterogeneous or homogeneous ethylene- α -olefin copolymers, ethylene-vinyl acetate co-polymers, ethylene-(C₁-C₄)alkyl acrylate or methacrylate co-polymers, ethylene-acrylic acid co-polymers, ethylene-methacrylic acid co-polymers, and blends thereof in any proportion.
- 20 10. A process for the manufacture of a bi-axially oriented, thermoplastic film comprising a first outer layer comprising a polyester or a copolyester, a second outer layer comprising an ethylene homo- or co-polymer, and a core layer comprising an ethylene-vinyl alcohol copolymer, said film being characterized by a modulus higher than 6,000 kg/cm² in at least one direction, which process
25 comprises co-extruding the film resins through a flat die and bi-axial orientating the obtained cast sheet simultaneously in the two perpendicular directions at an orientation ratio in the longitudinal direction higher than 2.5:1, preferably higher

than 3:1, and at an orientation ratio in the cross-wise direction higher than 2.5:1, preferably higher than 3:1, by means of a tenter frame, said process being optionally followed by an annealing or heat-setting step.

5

10

ABSTRACT

The invention relates to a bi-axially oriented film comprising a first outer layer comprising a polyester or a copolyester, a second outer layer comprising an ethylene homo- or co-polymer and a core layer comprising an ethylene-vinyl alcohol copolymer,
5 characterised by a modulus higher than $6,000 \text{ kg/cm}^2$ in at least one direction, obtained by a simultaneous biaxial orientation by means of a tenter frame. The films of the invention, when heat-shrinkable, also have a remarkably low shrink tension in the transverse direction.

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